

SHORT COMMUNICATION

PRISTANE: A NORDITERPENE HYDROCARBON FROM BUTE INLET WAX

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Abstract—Spectroscopic evidence is presented to prove the identity of a norditerpene hydrocarbon, isolated from Bute Inlet wax, with pristane (2,6,10,14-tetramethylpentadecane).

INTRODUCTION

BUTE Inlet is one of the larger fiords of the west coast of British Columbia and discharges into the complicated system of channels lying between the mainland and Vancouver Island at the north end of the Gulf of Georgia. Large quantities of wax of jelly-like consistency appear in this area and nearby waters during extremely cold winters and the wax disappears in water as soon as the temperature rises.¹ In this Laboratory, we have initiated a systematic chemical examination of this wax† whose origin is still a subject of various conjectures.¹

RESULTS AND DISCUSSION

We herein report the isolation and identification of a hydrocarbon (b.p. 152°/6.0 mm, n_D^{21} 1.4393, i.r. spectrum: 1170 cm^{-1} band with a shoulder at 1155 cm^{-1} and a strong doublet at 1365 and 1385 cm^{-1} (isopropyl group), no >C=C< vibrations) isolated by means of repeated column chromatography of the wax on silver nitrate impregnated silica gel (overall yield: 1.5 per cent).

The empirical formula $\text{C}_{19}\text{H}_{40}$ of Bute hydrocarbon was established by elementary analysis (Found: C, 84.74; H, 15.18. Calc.: C, 84.98; H, 15.02) and by high resolution mass spectrometry (observed mass 268.3125, calculated mass 268.3130). Its NMR spectrum was devoid of any olefinic signal, further confirmed by negative tetranitromethane test. Hence, it must be acyclic. GLC of this hydrocarbon on two different stationary phases suggested it to be homogeneous. Because of its short retention time in GLC (Table 1), this must be a branched hydrocarbon;² this premise being further supported by spectroscopic evidence (*vide infra*).

The mass spectrum of Bute hydrocarbon displayed a molecular ion peak at m/e 268 (0.59 per cent Σ_{27}) with a base peak at m/e 57 (14.27 per cent Σ_{27}). The fragmentation pattern with intense peaks in high mass region was quite characteristic of a branched hydrocarbon.^{3, 4}

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¹ M. Y. WILLIAMS, *Trans. Roy. Soc. Canada* **40**, 13 (1957).

² B. HALLGREN and S. LARSSON, *Acta Chem. Scand.* **17**, 543 (1963).

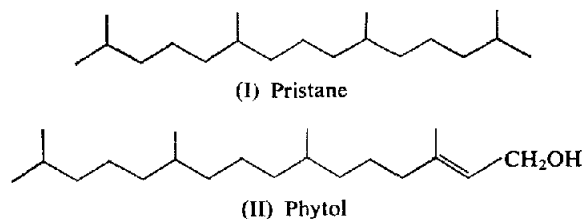
³ R. RYHAGE and E. STENHAGEN, *J. Lipid Res.* **1**, 361 (1960).

⁴ H. BUDZIKIEWICZ, C. DJERASSI and D. H. WILLIAMS, in *Mass Spectrometry of Organic Compounds*, p. 50, Holden-Day, San Francisco (1967).

TABLE I. RETENTION TIMES RELATIVE TO HEXADECANE

Sample	Methylphenylsilicone	Apiezon L
Hexadecane	1.00	1.00
Octadecane	1.94	2.27
Nonadecane	2.69	3.41
Bute hydrocarbon	1.34	1.44
2,6,10,14-Tetramethylpentadecane	1.35	1.43

Significant peaks occurred at m/e 113 (4.55 per cent Σ_{27}) and 183 (4.08 per cent Σ_{27}) which correspond respectively to $C_8H_{17}^+$ (observed mass 113.1328, calculated mass 113.1330) and $C_{13}H_{27}^+$ (observed mass 183.2110, calculated mass 183.2113). These fragments could arise only if the methyl groups are located at C_6 and C_{10} in the chain. The NMR spectrum of Bute hydrocarbon displayed a sharp 18-proton doublet at 9.14 τ ($J=5.7$ c/s) accounting for six secondary methyl groups in the molecule. Biogenetic considerations for isoprenoids coupled with spectral data enabled us to deduce the location of the remaining four methyl groups as depicted in structure I for Bute hydrocarbon which must be identical with norphytane synthesized from phytol (II) by Sørensen.⁵ These workers were able to prove the identity between synthetic norphytane (2,6,10,14-tetramethylpentadecane) and pristane.⁶ Finally, a direct comparison of the i.r., NMR and mass spectra and GLC behaviour of Bute hydrocarbon I with the corresponding spectra and GLC behaviour of an authentic specimen of 2,6,10,14-tetramethylpentadecane proved that they were identical in all respects.



It may be relevant to point out the recent report that phytol (II) itself is the precursor of the interesting hydrocarbon I, which may have originated in a prehistoric era.^{7, 8} We are currently investigating the oxygenated constituents of Bute Inlet wax which will eventually be of great value in establishing the origin of this wax.

EXPERIMENTAL

NMR spectra were obtained with a Varian Associates HA-60 spectrometer; i.r. spectra were run on Perkin-Elmer Infracord, Model 337, calibrated with polystyrene film; mass spectra were recorded on A.E.I. MS-9 and Hitachi-Perkin-Elmer RMU-6E mass spectrometers. All GLC analyses were carried out on a Perkin-

⁵ J. S. SØRENSEN and N. A. SØRENSEN, *Acta Chem. Scand.* **3**, 939 (1949).

⁶ J. PLIVA and N. A. SØRENSEN, *Acta Chem. Scand.* **4**, 846 (1950).

⁷ H. J. NICHOLAS, in *Biogenesis of Natural Compounds* (edited by P. BERNFELD), p. 866, Pergamon Press, New York (1967).

⁸ J. G. BENDORAITIS, B. L. BROWN and L. S. HEPNER, *Anal. Chem.* **34**, 49 (1962).

Elmer Gas Chromatograph, Model 810 (with flame ionization detector), equipped with 6 ft \times 0.25 in. columns operated at 209° (methyl phenyl silicone) and 221° (Apiezon L) with 28 ml of helium/min as a carrier gas.

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